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Review

Selective Halogenation and Pseudohalogenation*

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Recent studies on addition of halogens, interhalogens, and pseudohalogens to alkenes and alkynes, substitution of hydrogen by halogens in alkane and benzene derivatives, and replacement of halogens of alkyl halides by thiocyanato, all of which proceed with high stereo- and/or regio-selectivities, are reviewed.

KEY WORDS: Halogenation/ Pseudohalogenation/ Alkenes/ Alkynes/ Arenes/

Some excellent reviews[1] are available concerning the direct introduction of halogen or pseudohalogen species into organic substrates by addition or substitution. The general and theoretical aspects on these reactions can be found in most of these reviews. In this review article, therefore, some recent studies related to stereo- and/or regio-selective halogenation and pseudohalogenation are summarized concisely from synthetic viewpoint.

I. *Addition of Halogens to Alkenes and Alkynes*

It has been well-known that the addition of I_2 or Br_2 to aliphatic alkenes and alkynes in solvents of low polarity generally affords the *anti* adducts almost exclusively, whereas in the addition of Cl_2 involving a weakly bridged ion as the product-determining intermediate the adducts are formed with somewhat lower stereospecificity. For aryl-substituted alkenes, Br_2 adds in *anti* mode with considerable stereospecificity, but the addition of Cl_2 shows an excess of *syn* addition suggesting a carbenium-chloride ion pair intermediate.[2,3] Though an open vinyl cation intermediate is generally assumed for the halogenation of aryl-substituted alkynes, the reaction proceeds with considerable *anti* stereoselectivity except for the addition of Cl_2, so far as the reaction is carried out in solvents of low polarity.[5,6,7] Recent stereochemical data on the halogenation of some alkenes and alkynes are shown in Table I. In the bromide-catalyzed bromination of olefins and acetylenes which probably proceeds through a termolecular mechanism, a considerable increase in the proportion of the *anti* adducts has been known. Recently the use of Br_2-crown ether or Br_2-pyridine complexes in the place of Br_2 is recommended to improve

* This review article was accepted on the occasion of the retirement of Professor Emeritus Yuzo Inouye and is dedicated to him.

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Table I. Stereochemistry of Halogenation of Some Alkenes and Alkynes with Halogens.

Substrate	Halogen	Solv. and Temp. (°C)	*anti*-Adduct (%) in Dihalide	Ref.
t-PhCH=CHMe	Br_2	CCl_4, 2–5	88	2
c-PhCH=CHMe	Br_2	CCl_4, 2–5	83	2
t-PhCH=CHMe	Cl_2	CCl_4, 0–5	45[a]	3
c-PhCH=CHMe	Cl_2	CCl_4, 0–5	32[b]	3
t-PhCH=CHMe	F_2	CCl_3F, −78	31	4
c-PhCH=CHMe	F_2	CCl_3F, −78	22	4
n-$C_6H_{13}C\equiv CH$	Br_2	$CHCl_3$, 48	96	5
$PrC\equiv CPr$	Br_2	$CHCl_3$, 20	100	5
$EtC\equiv CEt$	Cl_2	CCl_4, 35	96	6
$PhC\equiv CH$	I_2	$CHCl_3$, 60	100	7
$PhC\equiv CPh$	I_2+MeCO_3H	AcOH-Et_2O, 25	100	8
$PhC\equiv CH$	Br_2	$CHCl_3$, 20	85	5
$PhC\equiv CEt$	Br_2	$CHCl_3$, 20	86	5
$PhC\equiv CH$	Cl_2	CCl_4, 0	49	6
$PhC\equiv CEt$	Cl_2	CCl_4, 0	50	6

a) Other product, *c*-PhCH=C(Cl)Me. Dichloride: monochloride=84: 16.
b) Other product, *t*-PhCH=C(Cl)Me. Dichloride: monochloride=95: 5.

Table II. Effects of Solvents and Additives on Stereochemistry of Bromination of *β*-Methylstyrene and Phenylacetylene.

Substrate	Halogenating Agent	Solvent (*ε*)	*anti*-Adduct (%) in Dibromide	Ref.
t-PhCH=CHMe	Br_2	C_6H_{12} (2.0)	92	9
	Br_2-DBC[a]	C_6H_{12}	100	9
	Br_2	AcOH (6.2)	83[b,c]	10
	Br_2-LiBr	AcOH	95[b,d]	10
	Br_2	CH_2Cl_2 (8.9)	89	11
	Br_2-pyridine	CH_2Cl_2	98	11
	Br_2-DBC	CH_2Cl_2	100	9
c-PhCH=CHMe	Br_2	C_6H_{12}	85	9
	Br_2-DBC	C_6H_{12}	100	9
	Br_2	AcOH	73[b,c]	10
	Br_2-LiBr	AcOH	95[b,d]	10
	Br_2	CH_2Cl_2	75	11
	Br_2-PyHBr	CH_2Cl_2	100	11
$PhC\equiv CH$	Br_2-$LiClO_4$	AcOH	52[e]	12
	Br_2-LiBr	AcOH	>99	12

a) Dibenzo-18-crown-6.
b) Other product, $PhCH(OAc)CH_2Br$.
c) Dibromide: bromoacetate=*ca.* 75–80: 20–25.
d) Dibromide: bromoacetate=*ca.* 85: 15.
e) Other products; *E*- & Z-Ph(OAc)C=CHBr and $PhCOCHBr_2$. Dibromide: other products=73: 27.

the *anti* selectivity in the bromination of aryl-substituted alkenes and alkynes (Table II).[9,11] Further, it is found that the radical chlorination of alkyl and aryl alkynes with Cl_2, SO_2Cl_2, or benzene iododichloride appears to be efficient for the selective formation of the corresponding *E*-dichlorides (Table III).[6,13,14] It should be noted here that the possibility of a change in the ratio of the *E*- and *Z*-isomer due to prolonged reaction is sometimes present.

Table III. Stereochemistry of Radical Chlorination of β-Methylstyrene and Some Alkynes.

Substrate	Halogenating Agent	Solv. and Temp. (°C)	*anti*-Adduct (%) in Product	in Equilibrium	Ref.
t-PhCH=CHMe	$PhICl_2$[a]	$CHCl_3$, 60	94	—	13
c-PhCH=CHMe	$PhICl_2$[a]	$CHCl_3$, 60	6	—	13
n-$C_6H_{13}C{\equiv}CH$	Cl_2, hν	CCl_4, 0	94		6
	$PhICl_2$[a]	$CHCl_3$, 60	94	53	6
	SO_2Cl_2	C_6H_6, 80	93		14
$PhC{\equiv}CH$	Cl_2, hν	CCl_4, 0	83		6
	$PhICl_2$[a]	$CHCl_3$, 60	89	14	6
	SO_2Cl_2	C_6H_6, 80	85		14
$PhC{\equiv}CEt$	Cl_2, hν	CCl_4, 0	75		6
	SO_2Cl_2	C_6H_6, 80	75		14
$PhC{\equiv}CPh$	$PhICl_2$[a]	$CHCl_3$, 60	76	28	6

a) Azobisisobutyronitrile (radical initiator) is added.

Compared with halogenation by molecular halogens, some characteristics have been found in halogen addition by metal halides. For example, $SbCl_5$ or $MoCl_5$ reacts with alkenes and alkynes to afford the *syn* adducts predominantly.[15,16,21] On the contrary, the favorable formation of the *E*-dihalides from alkynes is found in the case of $CuBr_2$ or $CuCl_2$.[5,20] Recently, an efficient but rather complex *in situ* Mo(VI) reagent for the *syn* chlorination of alkenes has been developed.[17] Some data on the halogenation of alkenes and alkynes using metal halides are tabulated in Table IV. Halogenation by metal halides appears to be synthetically useful because highly stereoselective dichlorides or dibromides can be easily prepared.

A comparison of the halogenation of butadiene with Br_2 and Cl_2 has been carried out. The effect of solvent polarity on regioselectivity is somewhat significant in the bromination, whereas it is insensitive in the chlorination.[22] Butadiene reacts with Br_2 to give the 1,4-adduct with *trans* configuration mainly, but when Br_2-pyridine complex is used as a brominating agent the 1,2-adduct is formed predominantly.[11] On the other hand, its chlorination by Cl_2 yields a mixture of almost equal amounts of the 1,2- and 1,4-adducts, while the reaction with $SbCl_5$ at low temperatures is highly stereoselective toward the formation of the thermodynamically least stable product, *cis*-1,4-dichloro-2-butene.[23] Several data are shown in Table V. A lower regioselectivity in the Cl_2 addition compared to the Br_2 addition may be due to an extensive dispersal of positive charge into the vinylic system.[22] The

Table IV. Stereochemistry of Halogenation of Some Alkenes and Alkynes with Metal Halides.

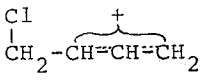
Substrate	Metal Halide	Solv. and Temp. (°C)	Yield (%)	*anti*-Adduct (%) in Product	Ref.
t-MeCH=CHMe	$SbCl_5$	CCl_4, 76	96	18	15
	$MoCl_5$	CCl_4, 76	85	16	16
c-MeCH=CHMe	$SbCl_5$	CCl_4, 76	98	16	15
	$MoCl_5$	CCl_4, 76	92	15	16
t-PrCH=CHPr	$(Bu_4N)_4Mo_8O_{26}$ +AcCl	CH_2Cl_2, 25	91	2	17
cyclo-C_6H_{10}	$MoCl_5$	CCl_4, −10∼0	70	2	18
t-PhCH=CHMe	$SbCl_5$	CCl_4, −10∼0	63	25	19
c-PhCH=CHMe	$SbCl_5$	CCl_4, −10∼0	67	0	19
n-$C_6H_{13}C\equiv CH$	$CuBr_2$	MeCN, 25	73	100	5
$PrC\equiv CPr$	$CuBr_2$	MeCN, 25	65	100	5
$PhC\equiv CH$	$CuBr_2$	MeCN, 25	77	97	5
$PhC\equiv C$-*i*-Pr	$CuBr_2$	MeCN, 25	60	91	5
$PhC\equiv C$-*t*-Bu	$CuBr_2$	MeCN, 25	100	9	5
n-$C_6H_{13}C\equiv CH$	$CuCl_2$-LiCl	MeCN, 82	83	92	20
$PrC\equiv CPr$	$CuCl_2$-LiCl	MeCN, 82	42	98	20
	$MoCl_5$	CH_2Cl_2, 25	37	3	18
$PhC\equiv CH$	$CuCl_2$-LiCl	MeCN, 82	71	94	20
$PhC\equiv CEt$	$SbCl_5$	CCl_4, 25	32	16	21
$PhC\equiv C$-*t*-Bu	$CuCl_2$-LiCl	MeCN, 82	94	21	20
	$SbCl_5$	CCl_4, 76	55	0	21

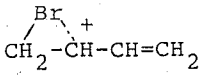
Table V. Product Distribution of Halogenation of Butadiene.

Halogenating Agent	Solv. and Temp. (°C)	Product Distribution (%) 1,2-	*t*-1, 4-	*c*-1, 2-	$\frac{\text{1, 2-Add.}}{\text{1, 4-Add.}}$	Ref.
Br_2	*n*-C_5H_{12}, −10	69	31	—	2.2	22
Br_2	CCl_4, −10	57	43	—	1.3	22
Br_2	CH_2Cl_2, −10	28	72	—	0.35	22
Br_2-Py	CH_2Cl_2, 0∼5	85	15	—	5.7	11
Br_2-Py+Py	CH_2Cl_2, 0∼5	96	4	—	24	11
Cl_2	*n*-C_5H_{12}, −10	55	45	—[a]	1.2	22
Cl_2	CCl_4, −10	57	43	—	1.3	22
Cl_2	CH_2Cl_2, −20∼−10	54	45	<1	1.2	23
$SbCl_5$	CH_2Cl_2, −26∼−13	35	25	40	0.54	23
$SbCl_5$	CH_2Cl_2, −22∼−12[b]	25	51	24	0.33	23
$CuCl_2$	CH_3CN, 60	15	80	5	0.18	33

a) The isomer ratio of dichlorobutenes in equilibrium (neat, at 60°C), 1, 2-: *t*-1, 4-: *c*-1, 4- =17: 77: 6 (Ref. 23).

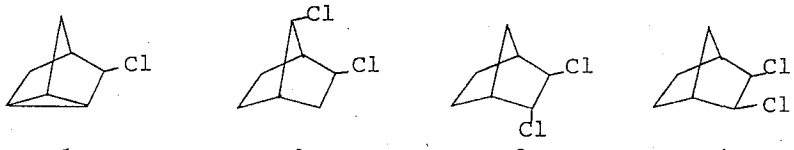
b) Reverse addition mode. Diene was added to $SbCl_5$ solution.





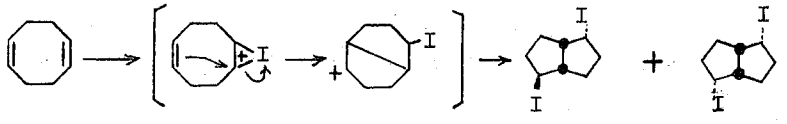
addition of Br_2 or Cl_2 to cyclopentadiene, a conjugated cyclic diene, affords the *syn*-1,4-adduct favorably,[24] but bromination by Br_2-pyridine complex yields the *anti*-1,2-adduct almost exclusively.[11]

It has been known already that the main products in the ionic chlorination of norbornene with Cl_2 are nortricyclyl chloride (**1**) and *exo*-2-*syn*-7-dichloronorbornane (**2**), and no appreciable formation of the 2,3-dichloro isomer is observed. A recent study shows that treatment with a mixture of $CuCl_2$ and LiCl in MeCN or with $MoCl_5$ or VCl_5 in CCl_4 affords mainly *trans*- or *cis*-2,3-dichloronorbornane (**3**, **4**), respectively, in good yields.[25] Interestingly, radical chlorination by SO_2Cl_2 or benzene iododichloride in CCl_4 also gives the *trans*-2,3-isomer favorably.[26,27]



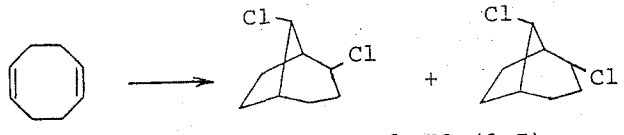
1 **2** **3** **4**

The halogenation of cyclic monoolefins and unconjugated cyclic dienes with molecular halogens is known to proceed in usual mode, *i.e.*, 1,2-*anti*-addition. However, it is found that in the chlorination of *cis*,*cis*-1,5-cyclooctadiene with $MoCl_5$ in CCl_4, or with SO_2Cl_2 or PCl_5 in refluxing CCl_4 the *cis*-1,2-dichloride is formed predominantly.[26,28] Further, though the reaction with Br_2 or Cl_2 gives the corresponding *trans*-1,2-dihalides, a similar treatment with I_2 in CCl_4 results in the formation of isomeric 2,6-diiodobicyclo[3.3.0]octanes (**5**) in good yields.[29] A similar



5 77% (1:1)

transannular cyclization is known in the iodination of *cis*, *trans*-cyclodecadiene.[30] In the chlorination of the above diene and *cis*-cyclooctene with $SbCl_5$ in CCl_4 at low temperature, the formation of unusual products is reported.[31] A slow addition of $SbCl_5$ to the diene gives mainly a mixture of *exo*- and *endo*-2-*anti*-8-dichlorobicyclo-[3.2.1]octanes (**6**), which is probably formed by a transannular cyclization and its subsequent isomerization. Here, the reverse addition affords usual transannular



6 72% (3:7)

products (**5**, I → Cl). In the case of *cis*-cyclooctene *cis*-1,4-dichlorocyclooctane is formed predominantly and this can be explained by a transannular 1,5-hydride

shift.

Some recent results relating to the stereo- and/or regio-chemistry of mixed halogenation of olefins and acetylenes are summarized in Table VI. Various interhalogen compounds are known, but they are usually unstable except for ICl. Therefore the reaction is generally carried out under the *in situ* generation of interhalogens. Here it should be noted that the use of the parent halogen is sometimes accompanied by the formation of homohalogenated product. For example, in the preparation of *vic*-bromochlorocyclohexane from cyclohexene, a considerable increase in the product selectivity has been observed, when KBr-$CuCl_2$ combination is used as a halogenating agent instead of Br_2-$CuCl_2$ couple.[33] In the iodochlorination of olefins, it is revealed that I_2-$CuCl_2$ or I_2-$SbCl_5$ system is very often superior to ICl in the yield and regioselectivity of the products, and that I_2-$SbCl_5$ couple is especially suitable for the halogenation of olefins bearing electron-withdrawing groups.[32] Recently, a new iodofluorinating agent, $MeIF_2$, prepared from MeI and XeF_2 with

Table VI. *Stereo- and Regio-chemistry of Mixed Halogenation of Some Alkenes and Alkynes.*

Substrate	Halogenating Agent	Solv. and Temp. (°C)	Yield (%)	*anti*-Adduct in Product (%)	M[a] in Product (%)	Ref.
$BuCH=CH_2$	ICl	CCl_4, 30	75		66	32
	I_2-$CuCl_2$	MeCN, 25	91		80	33
$CH_2=CHCl$	I_2-$CuCl_2$	MeCN, 50	81		73	33
$CH_2=CHOAc$	I_2-$CuCl_2$	MeCN, 25	83		100	33
$CH_2=CHCO_2Et$	I_2-$SbCl_5$	CCl_4, 76	86		18	32
t-$EtOOCCH=CHCO_2Et$	I_2-$SbCl_5$	CCl_4, 76	60	100	—	32
$PhCH=CH_2$	KI-$CuCl_2$	MeCN, 80	75		100	33
n-$C_6H_{13}CH=CH_2$	I_2-F_2	$CFCl_3$, −75	70		100	34
$BuCH=CH_2$	BrCl	CCl_4, 25	96		61	35
$CH_2=CHOAc$	Br_2-$SbCl_5$	CCl_4, 5	79		100	36
$CH_2=CHCO_2Me$	Br_2-Cl_2	CH_2Cl_2, 25	89		17	37
t-$EtOOCCH=CHCO_2Et$	Br_2-$SbCl_5$	CCl_4, 5	66	100	—	36
$PhCH=CH_2$	Br_2-$SbCl_3$	CCl_4, 0	87		100	36
	Br_2-AgF	C_6H_6, 0～25	71		100	38
$BuCH=CH_2$	NCS[b]-HF	HF-Py-Sulfolane, 25	40		100	39
n-$C_6H_{13}C\equiv CH$	ICl	MeCN, 82	50	100	100	20
	I_2-$CuCl_2$	MeCN, 82	84	100	100	20
$PhC\equiv CH$	ICl	MeCN, 82	52	95	100	20
	I_2-$CuCl_2$	MeCN, 82	97	100	100	20
$PhC\equiv CEt$	I_2-$CuCl_2$	MeCN, 82	100	100	100	20
$PhC\equiv CMe$	$MeIF_2$	MeI-HF, 25	70	0	100	40
$BuC\equiv CH$	BrCl	CCl_4, 25	79	100	90	35
$EtC\equiv CEt$	NBA[c]-HF	HF-Et_2O, −78～−20	48	95	100	41
	NBA-HF	HF-THF, −78～0	28	78	—	41

a) M; Markovnikov addition product. b) N-Chlorosuccinimide. c) N-Bromoacetamide.

HF catalyst, has been developed.[40] This reacts with aryl-substituted alkenes to form the expected Markovnikov adducts with high *anti*-stereospecificity, while with aryl-substituted alkynes it affords only the *syn* adducts as the kinetically controlled products.[40]

II. *Addition of Pseudohalogens to Alkenes and Alkynes*

Compared to halogens, thiocyanogen is known to be a weak electrophile. Thus, under heterolytic conditions, it reacts with olefins in solvents of low polarity to form two *anti*-stereospecific products, *i.e.*, α, β-dithiocyanates and α-isothiocyanato-β-thiocyanates, in which the latter formation is favored,[42,43] while it does not react with acetylenes. In the reaction with olefins, relative yields of dithiocyanates can be increased by the addition of catalytic amounts of Fe or $Fe(SCN)_3$.[42] On the contrary, under homolytic conditions, both alkenes and alkynes react with thiocyanogen readily. Simple alkenes afford the corresponding dithiocyanates with non-stereospecificity, while alkynes yield dithiocyanatoalkenes with high *anti*-stereoselectivity.[44,45] As in the case of dihalogenoalkenes, dithiocyanatoalkenes are also susceptible to subsequent thermodynamically-controlled isomerization. Several data are given in Table VII.

Table VII. Heterolytic and Homolytic Addition of Thiocyanogen to Some Alkenes and Alkynes.

Substrate	Solv. and Temp. (°C)	Yield (%)	Product Distribution (%) S-S[a] (*anti*-Adduct %)	S-N[a]	Ref.
t-EtCH=CHEt	MeCN, 25[b]	37	69(100)	31(100)	42
	C_6H_6, 25[b]	48	37(96)	63(98)	42
	C_6H_6, 25[b,c]	92	99.8(99)	0.2(100)	42
$Me_2C=CMe_2$	C_6H_6, 25[b]	90	33(100)	67(100)	43
$PhCH=CH_2$	C_6H_6, 25[b]	66	67	33	43
t-MeCH=CHMe	C_6H_6, hν, 20~30	99	100(60)		44
c-MeCH=CHMe	C_6H_6, hν, 20~30	94	100(39)		44
$PhCH=CH_2$	C_6H_6, hν, 20~30	99	100		44
$HC\equiv CH$	C_6H_6, hν, 20~25	90	100(95)		45
$EtC\equiv CEt$	C_6H_6, hν, 20~25	97	100(90)		45
$PhC\equiv CMe$	C_6H_6, hν, 20~25	90	100(89)		45
$PhC\equiv CPh$	C_6H_6, hν, 20~25	90	100(94)		45

a) S-S: Dithiocyanate. S-N: Isothiocyanatothiocyanate.
b) 2,6-Di-*t*-butyl-4-methylphenol (radical inhibitor) was added; in darkness.
c) $Fe(SCN)_3$ was added as catalyst.

It has been known that halogen azides can add to alkenes by either an ionic or free-radical mechanism. From the electronegativity trend $I<N_3\simeq Br<Cl$, it would be expected that the preference for an ionic mechanism would be $IN_3>BrN_3>ClN_3$. This is confirmed by comparison of the halogen azide addition to styrene under various conditions (Table VIII).[46] Here, the Markovnikov adducts are formed by ionic route and the *anti*-Markovnikov adducts by radical pathway.

Table VIII. Heterolytic and Homolytic Addition of Halogen Azides to Styrene.

Reagent	Solv. and Temp. (°C)	Product Distribution (%) M[a]	aM[b]	Ref.
IN_3 ($ICl+NaN_3$)	MeCN, 0	100	0	46
	n-C_5H_{12}, N_2, 0	61	39	46
BrN_3 (Br_2+NaN_3)	$MeNO_2$, N_2, 0	>96	<4	46
	n-C_5H_{12}, N_2, 0	0	100	46
ClN_3 (Cl_2+NaN_3)	$MeNO_2$, O_2, 0	48	17[c]	46
	n-C_5H_{12}, air, 0	0	100	46

a) Markovnikov adduct.
b) *anti*-Markovnikov adduct.
c) Other product, PhCH=CHCl (relative yield, 23%).

It is interesting that the nature of the reaction (*i.e.*, ionic or radical) is readily changed in the case of BrN_3.

In ionic media, ISCN is polarized in the manner $I^{\delta+}{}^{\delta-}SCN$, while BrSCN and ClSCN are in the reverse direction, *i.e.*, $X^{\delta-}{}^{\delta+}SCN$ (X=Br, Cl). When metal thiocyanates are used as a thiocyanogen source in the iodothiocyanation of olefins, product distribution varies significantly depending upon the metal salts. When KSCN is used *vic*-iodothiocyanates by *anti* addition are formed predominantly, while the use of TlSCN or $Hg(SCN)_2$ results in the favorable formation of *vic*-iodoisothiocyanates.[47,48] The halogenoselenocyanation of olefins can be readily accomplished in MeCN by using a redox system of KSeCN and CuX_2 (X=Br or Cl) as an *in situ* XSeCN reagent. The reaction proceeds with Markovnikov-type regioselectivity and with a high *anti*-stereospecificity to form halogenoselenocyanates exclusively.[50] Various data are shown in Table IX.

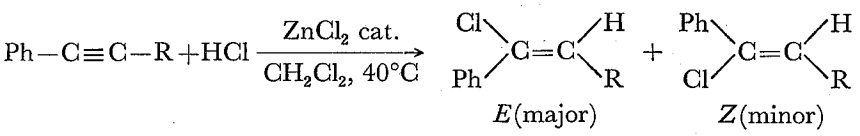
Table IX. Addition of Halogen Thiocyanates and Selenocyanates to Some Alkenes.

Substrate	Reagent	Solv. and Temp. (°C)	Yield (%)	Product Distribution (%) X-YCN[a]	X-NCY[a]	Ref.
cyclo-C_6H_{10}	I_2-KSCN	$CHCl_3$, 20	~100	96	4	47
	I_2-TlSCN	$CHCl_3$-sulfolane, 0	75	20	80	47
	I_2-$Hg(SCN)_2$	Et_2O, 20	80[b]	17	83	48
	I_2-$(SCN)_2$	C_6H_6, 20	72[b]	26	74	48
t-EtCH=CHEt	I_2-KSCN	Et_2O, 20	63	95	5	48
	I_2-$Hg(SCN)_2$	C_6H_6, 20	84	12	88	48
cyclo-C_6H_{10}	Br_2-TlSCN	$CHCl_3$, 25	51[c]	100	0	49
	$CuBr_2$-KSeCN	MeCN, 82	54	100	0	50
	$CuCl_2$-KSeCN	MeCN, 82	69	100	0	50
PhCH=CH_2	$CuBr_2$-KSeCN	MeCN, 82	58	100	0	50
	$CuCl_2$-KSeCN	MeCN, 82	83	100	0	50

a) X-YCN: Halogenothiocyanate (Y=S) or halogenoselenocyanate (Y=Se). X-NCY: Halogenoisothiocyanate (Y=S) or halogenoisoselenocyanate (Y=Se). All products consist of *anti*-adducts entirely or mostly.
b) Other product, Dithiocyanate (1%).
c) Other products, Dibromide (7%) and dithiocyanate (15%).

III. *Introduction of Halogen or Pseudohalogen into Aliphatic Compounds by Other Reactions*

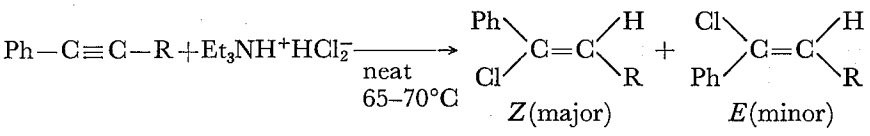
The stereochemistry of HCl addition to phenylacetylenes has recently been studied. The addition of HCl in CH_2Cl_2, in the presence of $ZnCl_2$, proceeds with high *syn*-stereoselectivity, indicating the initial formation of an open vinyl cation intermediate and the subsequent preferential attack of Cl^- from the less hindered



E(major) Z(minor)

R=D 85% (E/Z=7/3); R=Et 40% (E/Z=8/2); R=*t*-Bu 79% (only E)

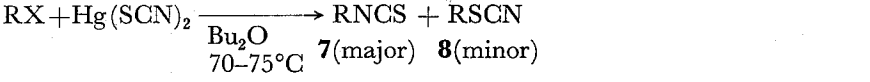
site.[51] On the other hand, the hydrochlorination by $Et_3NH^+HCl_2^-$ without catalyst yields the *anti*-adducts predominantly, probably through a trimolecular mechanism.[52]



Z(major) E(minor)

R=H 73%; R=Me 36% (Z/E=89/11)

The reaction of alkyl and aralkyl halides with KSCN in dipolar aprotic solvents is well-known as a preparative method of the corresponding thiocyanates. Based on the HASB principle, it would be expected that the predominant formation of iothiocyanate is achieved by a suitable choice of metal thiocyanates and/or solvents. In fact, it is found that when secondary or tertiary halides are treated with $Hg(SCN)_2$ in solvents of low polarity (*e.g.*, *n*-hexane or di-*n*-butyl ether), the corresponding isothiocyanates are obtained with high selectivity.[53] A mechanism



7(major) **8**(minor)

X=I, R=*i*-Pr 72% (**7**/**8**=85/15); X=Br, R=*t*-Bu 68% (**7**/**8**=96/4);
X=Br, R=PhCHMe 87% (**7**/**8**=99/1)

involving the initial Hg-catalyzed ionization of alkyl halide and simultaneous formation of the complex ion $[XHg(SCN)_2]^-$, followed by the attack of the terminal N site of this anion to alkyl cation, is proposed.

The introduction of halogen species at a definite position of long *n*-alkyl chain seems to be principally difficult, but the following finding is quite attractive from synthetic viewpoint. When C_6-C_8 aliphatic alcohols and acids are treated with sterically hindered *N*-chlorodiisopropylamine in conc. H_2SO_4 under irradiation, the chlorination occurs at the ω-1 position of the substrates with high selectivity.[54] An extention of this study to C_8-C_{12} dicarboxylic acids has also been reported.[55] In these reactions, an electrostatic repulsion between the protonated group (*e.g.*,

$COOH_2^+$) and the attacking radical cation ($R_2NH^{+\cdot}$) would be operative.

$$CH_3(CH_2)_5OH \xrightarrow[74\%\ H_2SO_4]{(i\text{-}Pr)_2NCl,\ h\nu} CH_3\underset{Cl}{CH}(CH_2)_4OH + CH_2\underset{Cl}{(CH_2)_5OH} + \overset{other}{C_6H_{12}Cl(OH)}$$

(ratio=90:6:4)

$$CH_3(CH_2)_6CO_2H \xrightarrow[84\%\ H_2SO_4]{(i\text{-}Pr)_2NCl,\ h\nu} CH_3\underset{Cl}{CH}(CH_2)_5CO_2H + C_2H_5\underset{Cl}{CH}(CH_2)_4CO_2H$$

$$\overset{other}{+C_7H_{14}Cl(CO_2H)} \quad \overset{total\ yield\ 90\%}{(ratio=80:14:6)}$$

$$HOOC(CH_2)_7CO_2H \xrightarrow[85\%\ H_2SO_4]{(i\text{-}Pr)_2NCl,\ h\nu} HOOC(CH_2)_3\underset{Cl}{CH}(CH_2)_3CO_2H$$

$$+HOOC(CH_2)_2\underset{Cl}{CH}(CH_2)_4CO_2H + \overset{other}{C_7H_{13}Cl(CO_2H)_2}$$

total yield 72% (ratio=58:40:2)

$$HOOC(CH_2)_{10}CO_2H \xrightarrow[95\%\ H_2SO_4]{(i\text{-}Pr)_2NCl,\ h\nu} HOOC(CH_2)_4\underset{Cl}{CH}(CH_2)_5CO_2H$$

$$+HOOC(CH_2)_3\underset{Cl}{CH}(CH_2)_6CO_2H + \overset{other}{C_{10}H_{19}Cl(CO_2H)_2}$$

(ratio=72:27:1)

IV. *Halogenation and Pseudohalogenation of Benzene Nucleus*

Phenols, phenyl ethers, and anilines are readily halogenated, and usual halogenation by molecular halogens generally affords a mixture of *o*- and *p*-halogenated, and/or polyhalogenated compounds. A redox combination I_2-$CuCl_2$ has been developed as a simple and gentle iodinating reagent for aromatics, and in the iodination of phenol, anisole, and *N,N*-dimethylaniline with this reagent only the *para*-iodo-substituted products are formed.[56] For the introduction of I into the *ortho*-position of phenols, I_2-TlOAc is found to be appropriate.[57] However, for anisole and anilines, this reagent leads to only *para*-substitution. Though the predominant *para*-bromination of phenols with Br_2 in various solvents has been known, it is reported that in CCl_4 or $CHCl_3$ solvent *N*-bromosuccinimide (NBS) brominates phenols in the *ortho*-position with high selectivity, but in polar aprotic solvents the reaction is *para*-selective.[58] The use of NBS in DMF is quite useful for the selective monobromination of reactive aromatics including polynuclear hydrocarbons.[59] Recently, it is also found that, in HF-SbF_5, *p*-cresol and xylenols react with Br_2 to give the corresponding *meta*-bromo-substituted compounds in good yields, indicating the bromination of the O-protonated substrate.[60] This method is not applicable to

phenol, *o*- and *m*-cresol, all of which afford only the *para*-substitution products. In contrast to the halogenation of phenol with I_2 and Br_2, the effect of solvent on the product ratio appears to be significant in the chlorination by Cl_2. For example, the *o*:*p* ratio is 0.49 (in EtOH, phenol conc. 10 wt%, at 78°C), 0.65 (neat, at 60°C) and 2.5 (in CCl_4, phenol conc. 5 wt%, at 78°C). A selective *para*-chlorination of phenol has been achieved by using $CuCl_2$ in DMF.[61] In the regioselective *para*-chlorination of *o*-cresol with SO_2Cl_2, the addition of diphenyl sulfide and $AlCl_3$ is effective for an improvement of the selectivity.[63] In the chlorination of anisole with Cl_2, the *o*:*p* ratio is known to be 0.25 in CCl_4, but the use of nitromethane as solvent appears to increase the *para*-selectivity.[62] Recently, the chlorination of phenols with good regioselectivity is achieved by using a suitable polychlorohexadienone. Phenol reacts with 2,3,4,4,5,6-hexachlorocyclohexa-2,5-dien-1-one to give *p*-chlorophenol predominantly, and with 2,3,4,5,6,6-hexachlorocyclohexa-2,4-dien-1-one to afford *o*-chlorophenol preferentially. The reaction appears to proceed *via* a charge transfer complex in which phenol acts as both π-donor and proton donor and the dienone as π-acceptor and proton acceptor.[64] Several data on selective halogenation of phenols and anilines are shown in Table X.

The halogenation of moderately active and less active aromatics with molecular halogens is mostly carried out in the presence of a catalyst. However, the use of

Table X. Selective Halogenation of Phenols and Anilines.

Substrate	Halogenating Agent	Solv. and Temp. (°C)	Products (Total yields (%) & their ratio)	Ref.
PhOH	I_2-$CuCl_2$	PhCl, 130	*p*-IC_6H_4OH (69)	56
$PhNMe_2$	I_2-$CuCl_2$	C_6H_6, 60	*p*-$IC_6H_4NMe_2$ (47)	56
PhOH	I_2-TlOAc	AcOH, 20	*o*-IC_6H_4OH (60)	57
	Br_2	CCl_4, 25	*o*- & *p*-BrC_6H_4OH (>95, 11:89)	58
	NBS[a]	CCl_4, 25	*o*- & *p*-BrC_6H_4OH (>95, 86:14)	58
	NBS	MeCN, 25	*o*- & *p*-BrC_6H_4OH (>95, 3:97)	58
	NBS	DMF, 25	*p*-BrC_6H_4OH (70)	59
m-MeC_6H_4OH	NBS	DMF, 25	4-Br-3-MeC_6H_3OH (89)	59
$PhNH_2$	NBS	DMF, 25	*p*-$BrC_6H_4NH_2$ (93)	59
p-MeC_6H_4OH	Br_2	HF-SbF_5, 45	3-Br-4-MeC_6H_3OH (85)	60
3,4-$Me_2C_6H_3OH$	Br_2	HF-SbF_5, 45	5-Br-3,4-$Me_2C_6H_2OH$ (83)	60
PhOH	$CuCl_2$-LiCl	DMF, 150	*o*- & *p*-ClC_6H_4OH (60, 1~2:8~9)	61
PhOMe	Cl_2	$MeNO_2$-CH_2Cl_2, 0	*o*- & *p*-ClC_6H_4OMe (96, 1:9)	62
o-MeC_6H_4OH	SO_2Cl_2	neat, 25	2- & 4-Cl-6-MeC_6H_3OH (97, 1:6.2)	63
	SO_2Cl_2-Ph_2S-$AlCl_3$	neat, 15	2- & 4-Cl-6-MeC_6H_3OH (99, 1:19)	63
PhOH	*p*-hexachlorodienone[b]	DMF, 20	*o*- & *p*-ClC_6H_4OH (~100, 27:73)	64
	o-hexachlorodienone[c]	CCl_4, −5	*o*- & *p*-ClC_6H_4OH (~100, 92:8)	64

a) N-Bromosuccinimide. b)  c) 

Table XI. Selective Halogenation of Aromatics with Metal Halides.

Substrate	Metal Halides	Solv. and Temp. (°C)	Products (Total yield (%) & their ratio)	Ref.
PhBr	I_2-$SbCl_5$	CCl_4, 76	*p*-IC_6H_4Br (73)	65
PhF	I_2-$SbCl_5$	CCl_4, 76	*o*- & *p*-IC_4H_4F (74, 2:98)	65
$PhCO_2Et$	I_2-$SbCl_5$	$ClCH_2CH_2Cl$, 84	*m*-$IC_6H_4CO_2Et$ (48)	65
PhBr	Br_2-$SbCl_5$	CCl_4, 76	*o*- & *p*-$Br_2C_6H_4$ (86, 5:95)	65
PhCl	Br_2-$SbCl_5$	CCl_4, 76	*o*- & *p*-BrC_6H_4Cl (84, 4:96)	65
$PhNO_2$	Br_2-$SbCl_5$	$ClCH_2CH_2Cl$, 84	*m*-$BrC_6H_4NO_2$ (63)	65
PhMe	$FeCl_3$	neat, 40	*o*- & *p*-ClC_6H_4Me (71, 1:5)	66
	$FeCl_3$-$MoCl_4$	neat, 50	*o*- & *p*-ClC_6H_4Me (85, 1:12)	66
	$FeCl_3$-$TiCl_4$	neat, 50	*o*- & *p*-ClC_6H_4Me (83, 1:10.5)	66
PhCl	$FeCl_3$	neat, 115	*o*- & *p*-$Cl_2C_6H_4$ (94, 1:12)	66
	$FeCl_3$-$MoCl_4$	neat, 115	*o*- & *p*-$Cl_2C_6H_4$ (86, 1:19.5)	66
	$FeCl_3$-$TiCl_4$	neat, 105	*o*- & *p*-$Cl_2C_6H_4$ (99, 1:20.5)	66
PhMe	$TiCl_4$-CF_3CO_3H	CH_2Cl_2, 20	*o*- & *p*-ClC_6H_4Me (90, 85:15)	67
PhPh	$TiCl_4$-CF_3CO_3H	CH_2Cl_2, 20	2- & 4-ClC_6H_4Ph (76, 80:20)	67

metal halides (involving interhalogens formed *in situ* from metal halides) frequently leads to a significant improvement of the regioselectivity and/or yield of the products. Some recent data on the selective halogenation of aromatics by means of metal halides are collected in Table XI. Equimolar mixtures of I_2 or Br_2 and $SbCl_5$ are found to be elegant reagents for the iodination or bromination of less reactive aromatics such as benzoic ester and nitrobenzene. Further, *p*-iodo- or *p*-bromohalogenobenzenes can be prepared by these reagents with high selectivities.[65] In the chlorination of toluene with Cl_2, the *o*:*p* ratio varies with solvent considerably; for example, the ratio is 1.5 in AcOH and 0.52 in CH_3NO_2. When $FeCl_3$ is used as a chlorinating agent without solvent, the ratio decreases to 0.2. Recently, in the chlorination of toluene and chlorobenzene with $FeCl_3$, the addition of $MoCl_4$ or $TiCl_4$ is found to result in a remarkable increase in the proportion of *p*-substituted products.[66] On the contrary, for toluene and biphenyl, $TiCl_4$ can act as an *ortho*-selective halogenating agent in the presence of trifluoroperacetic acid.[67] In this case, the true reagent appears to be HOCl, though the observed *o*:*p* ratio (5.7) for toluene is somewhat higher than that (3.2) in the HOCl chlorination.

Compared to Cl_2, F_2 is much more reactive and there appears to be less selective as electrophile. This is recently confirmed by examining both orientation and relative rate in the F_2 fluorination of aromatics (in $CFCl_3$ at -78°C).[68] For introduction of SCN into moderately active aromatics, *in situ* BrSCN or ClSCN reagent, which is more reactive than $(SCN)_2$, is used in the presence of a Lewis acid.[69,70] In the thiocyanation of alkylbenzenes and halogenobenzenes with a mixture of $Pb(SCN)_2$ and $SbCl_5$ (equivalent to *in situ* ClSCN and $SbCl_5$), predominant *para*-substitution is observed (for example, the *o*:*p* ratio for ethylbenzene is 0.36 in CCl_4).[70] The selenocyanation of aniline is achieved by the use of $Cu(OAc)_2$-NaSeCN mixture and only the *para*-substitution product is isolated, but the procedure is not applicable to other active aromatics such as phenol and anisole.[71]

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